

What is claimed is:

[c01] A method for recovering a metal catalyst for reuse, wherein said metal catalyst is selected from the group consisting of elemental copper, copper compounds, and one or more compounds or complexes of Group IV-VIII transition metals of the Periodic Table of Elements, wherein said method comprises:

- (a) providing a reaction product mixture by contacting a hydroxyaromatic compound with oxygen and a bromine compound selected from the group of hydrogen bromide, elemental bromine, ionic bromide salts, and mixtures thereof, in an acidic medium and in the presence of said metal catalyst; and
- (b) removing a portion of said reaction product mixture without removing said metal catalyst.

[c02] The method of claim [c01], wherein said reaction product mixture comprises an organic phase and an aqueous phase, said aqueous phase comprising said metal catalyst, and wherein said portion of said product mixture being removed in step (b) is said organic phase.

[c03] The method of claim [c02], further comprising after step (b) the step of removing at least a portion of water from said aqueous phase without removing said metal catalyst.

[c04] The method of claim [c02], further comprising after step (b) the step of concentrating said aqueous phase into a solid wherein said solid comprises said metal catalyst.

[c05] The method of claim [c01], wherein said product mixture further comprises a volatile organic solvent.

[c06] The method of claim [c01], further comprising the step of concentrating the remaining product mixture into a solid wherein said solid comprises said metal catalyst.

[c07] A method of preparing a para-brominated hydroxyaromatic compound by an oxybromination reaction, said method comprising:

- (a) contacting in a reaction mixture a hydroxyaromatic compound with oxygen and a bromine compound selected from the group of hydrogen bromide, elemental bromine, ionic bromide salts, and mixtures thereof, in an acidic medium, in the presence of a metal catalyst selected from the group consisting of elemental copper, copper compounds, and one or more compounds or complexes of Group IV-VIII transition metals of the Periodic Table of Elements, to produce a two-phase reaction product mixture comprising an organic phase and an aqueous phase, wherein said organic phase comprises said para-brominated hydroxyaromatic compound, a corresponding ortho-brominated hydroxyaromatic compound, and unreacted said hydroxyaromatic compound, and wherein said aqueous phase comprises said metal catalyst, unreacted said bromine compound, and said acidic medium;
- (b) separating said organic phase of said product mixture from said aqueous phase, followed by optionally removing at least a portion of water from said aqueous phase; and
- (c) recycling at least a portion of said metal catalyst in said aqueous phase from which at least a portion of water has optionally been removed, to a further oxybromination reaction of additional said hydroxyaromatic compound employing oxygen and said bromine compound in said acidic medium.

[c08] The method of claim [c07], wherein said hydroxyaromatic compound is selected from the group consisting of phenol, o-cresol, and m-cresol, wherein aqueous hydrogen bromide is said acidic medium and said bromine compound, wherein oxygen in the form of pressurized air is employed, and wherein said metal catalyst is cupric bromide (CuBr_2).

[c09] The method of claim [c07], further comprising the step of removing said para-brominated hydroxyaromatic compound from said organic phase.

[c10] The method of claim [c07], wherein step (c) further comprises the step of recycling said unreacted said bromine compound, said acidic medium, and any residual said unreacted said hydroxyaromatic compound in said aqueous phase to said further oxybromination reaction.

[c11] The method of claim [c07], further comprising prior to step (c) the steps of:

- (i) washing said organic phase with water at least one time to remove any traces of unreacted bromine compound and any traces of said metal catalyst;
- (ii) removing said wash water from said organic phase;
- (iii) combining said wash water with said aqueous phase, and optionally removing a portion of water from said combined aqueous phase and wash water; and
- (iv) recycling said combined aqueous phase and wash water, wherein a portion of water has optionally been removed, in step (c) to said further oxybromination reaction.

[c12] The method of claim [c07], further comprising after step (b) the steps of

- (i) removing a stream from said organic phase comprising said corresponding ortho-brominated hydroxyaromatic compound;
- (ii) contacting said stream with additional said hydroxyaromatic compound and aqueous hydrogen bromide to form a pre-equilibration mixture; and
- (iii) heating said pre-equilibration mixture at a temperature ranging from about 25°C to about 200°C to form a post equilibration solution comprising said corresponding ortho-brominated hydroxyaromatic compound, said para-brominated hydroxyaromatic compound, unused said hydroxyaromatic compound, and said aqueous hydrogen bromide.

[c13] The method of claim [c12], further comprising the step of recycling said post-equilibration solution to a further oxybromination reaction of said unused hydroxyaromatic compound and additional said hydroxyaromatic compound employing said metal catalyst, oxygen, and said aqueous hydrogen bromide as said bromine source and said acidic medium.

[c14] The method of claim [c12], wherein said stream further comprises said para-brominated hydroxyaromatic from said organic phase.

[c15] The method of claim [c12], wherein said stream further comprises said unreacted hydroxyaromatic compound from said organic phase.

[c16] The method of claim [c12], further comprising the step of removing said para-brominated hydroxyaromatic compound from said post equilibration solution.

[c17] The method of claim [c12], wherein aqueous hydrogen bromide is said bromine compound and said acidic medium, and wherein said aqueous hydrogen bromide in step (ii) is provided by removing said unreacted aqueous hydrogen bromide from said aqueous phase and recycling said removed unreacted aqueous hydrogen bromide in step (ii).

[c18] A method of preparing a para-brominated hydroxyaromatic compound by an oxybromination reaction, said method comprising:

- (a) contacting in a reaction mixture a hydroxyaromatic compound with oxygen and a bromine compound selected from the group of hydrogen bromide, elemental bromine, ionic bromide salts, and mixtures thereof, in an acidic medium and in a volatile organic solvent, in the presence of a metal catalyst selected from the group consisting of elemental copper, copper compounds, and one or more compounds or complexes of Group IV-VIII transition metals of the Periodic Table of Elements, to produce a reaction product mixture comprising said metal catalyst and a product-containing liquid comprising said para-brominated hydroxyaromatic compound, a corresponding ortho-brominated hydroxyaromatic compound, unreacted said hydroxyaromatic compound, unreacted said bromine compound, said acidic medium, and said volatile organic solvent;
- (b) removing a major portion of said product-containing liquid from said reaction product mixture, wherein the removed major portion of said product-containing liquid comprises said corresponding ortho-brominated hydroxyaromatic compound, at least a portion of said para-brominated hydroxyaromatic compound, and a major portion of said unreacted hydroxyaromatic compound, and wherein the remaining said reaction product mixture comprises said metal catalyst and remaining said product-containing liquid comprising any residual para-brominated hydroxyaromatic compound, and residual said unreacted hydroxyaromatic compound; and

- (c) recycling at least a portion of said metal catalyst from said remaining reaction product mixture to a further oxybromination reaction of additional said hydroxyaromatic compound employing oxygen and said bromine compound in said acidic medium.

[c19] The method of claim [c18], wherein said hydroxyaromatic compound is selected from the group consisting of phenol, o-cresol, and m-cresol, wherein aqueous hydrogen bromide is said acidic medium and said bromine compound, wherein oxygen in the form of pressurized air is employed, and wherein said metal catalyst is cupric bromide (CuBr_2).

[c20] The method of claim [c18], wherein said aqueous hydrogen bromide is said acidic medium and said bromine compound, and wherein said method further comprises prior to step (b), the step of removing said unreacted said aqueous hydrogen bromide from said product-containing liquid and recycling said removed unreacted said aqueous hydrogen bromide to said further oxybromination reaction.

[c21] The method of claim [c18], further comprising after step (b) the step of removing at least a portion of said para-brominated hydroxyaromatic compound from said removed major portion of said product-containing liquid.

[c22] The method of claim [c18], further comprising prior to step (c) the steps of

- (i) washing said removed major portion of said product-containing liquid with water at least one time to remove any said unreacted bromine compound, any said acidic medium, and any traces of said metal catalyst;
- (ii) removing said wash water from said removed major portion of said product-containing liquid, and optionally removing a portion of water from said wash water; and
- (iii) recycling said wash water, wherein a portion of water has optionally been removed, in step (c) to said further oxybromination reaction.

[c23] The method of claim [c18], wherein said volatile organic solvent is selected from the group consisting of acetonitrile, chloroform, ethyl acetate, o-dichlorobenzene, acetic acid, and propionic acid.

[c24] The method of claim [c18], further comprising prior to step (b) the step of removing said polar organic solvent from said product-containing liquid and recycling said removed polar organic solvent to said further oxybromination reaction.

[c25] The method of claim [c18], further comprising after step (b) the steps of

- (i) removing a stream from said removed major portion of said product-containing liquid, wherein said stream comprises said corresponding ortho-brominated hydroxyaromatic compound;
- (ii) contacting said stream with additional said hydroxyaromatic compound and aqueous hydrogen bromide to form a pre-equilibration mixture; and

(iii) heating said pre-equilibration mixture at a temperature ranging from about 25°C to about 200°C to form a post equilibration solution comprising said corresponding ortho-brominated hydroxyaromatic compound and said para-brominated hydroxyaromatic compound, unused said hydroxyaromatic compound, and said aqueous hydrogen bromide.

[c26] The method of claim [c25], further comprising recycling said post-equilibration solution to a further oxybromination reaction of said unused hydroxyaromatic compound and additional said hydroxyaromatic compound employing said metal catalyst, oxygen, and said aqueous hydrogen bromide, as said bromine compound in said acidic medium.

[c27] The method of claim [c25], wherein said stream further comprises said para-brominated hydroxyaromatic from said removed major portion of said product-containing liquid.

[c27] The method of claim [c25], wherein said stream further comprises said major portion of said unreacted hydroxyaromatic compound from said removed major portion of said product-containing liquid.

[c28] The method of claim [c25], wherein said aqueous hydrogen bromide is said bromine compound in said acidic medium, and wherein said stream further comprises said unreacted said aqueous hydrogen bromide from said product-containing liquid.

[c29] The method of claim [c25], further comprising the step of removing said para-brominated hydroxyaromatic compound from said post equilibration solution.